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ON THE USE OF VOLTAMMETRIC DATA IN BIFURCATION ANALYSIS OF ELECTROCHEMICAL OSCILLATORY SYSTEM:Cu│1.0 M TFA

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ABSTRACT
Bifurcation analysis of the Cu│1 M TFA electrochemical oscillatory system was done by using voltammetric data, obtained under qusi-potetiostatic polarization conditions. Asuper-critical Hopf bifurcationand a saddle-loop bifurcation were identified at following bifurcation potentials E_{BIF1}= 0.5446 V andE_{BIF2}=0.7536 V, respectively.

INTRODUCTION
Beingfar-from-equilibrium, the electrochemical systems can spontaneously form a wide spectrum of spatio-temporal patterns [1, 2]. Spontaneous emergence of such patterns implies that the dynamical systems, such as electrochemical, undergo self-organization [2]. Appearance of oscillations implies that the electrochemical system can not longer achieve stable steady sates, and that its existence is only possible through oscillatory states [1].Transient from a stable steady state to an oscillatory state goes via bifurcation point. In order to be identified, evolution of the system has to be monitored through phase space diagram; constructed from a series of coordinates characterized bya parameter (controlled quantity) and a variable (quantity which is an appropriate representative of the systems state) [3,4].Looking from this perspective, linear sweep voltammetry can be observed as instrumental technique which dynamically drives the system throughout a series of variable-to-parameter points [5]. Therefore, voltammogram is in a fact a phase space diagram. In this study, a copper electrode in a trifluoroacetic acid (TFA) will be anodycally polarized by means of linear sweep voltammetry, under qusi-potetiostatic polarization conditions. Bifurcation analysis will be conduct by using voltammetric data.

EXPERIMENTAL

Experiments were carried out in a three-electrode electrolytic cell, at 293 K, with a copper rod (Goodfellow, 99.99%) as the working electrode, Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference one. The working electrode was embedded in a plastic capillary, leaving only the rod cross-section (0.0314 cm^2) exposed to the electrolyte solution. Prior to each experiment the working electrode was abraded by a series of wet sanding paper with different grit size (320, 600, 800, 1000, 1200 and 2000). Thereupon, the working electrode was rinsed with deionized water in an ultrasonic bath for 2 min. A Luggin capillary was used. Electrolyte solution was 1 M TFA. Experiments were carried under natural convection of electrolyte in the electrolytic cell, without any external resistance applied in the circuit. Linear sweep voltammetry was performed using anodic scan, starting from 0.5 V_{SCE}, at a rate of 1 mV s^{-1}. All applied circuit potentials (E)are given with the respect to the SCE.

RESULTS AND DISCUSSION

By carefully selection of initial conditions, we were able to locate an oscillatory state (OsS) region of investigated system at the current-potential (I-E)polarization curve, Fig.1.The first bifurcation point occurs at E_{BIF1}= 0.5446 V(looking from the direction of polarization). This bifurcation point can be observed as an entering one, markinga discontinuity in evolution of the system from the steady stable sate (SSS1) to OsS; it is a characteristic of the SSS1→OsS transient.

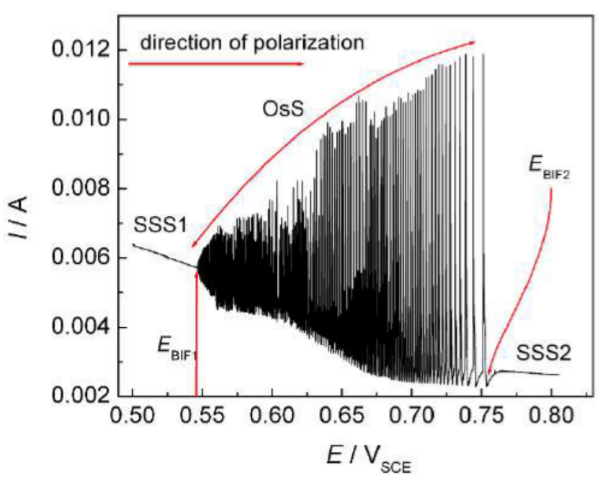

Figure 1. I-E polarization curve of Cu electrode in 1M TFA.

With respect to above mention perspective, the second bifurcation point, located at E_{BIF2}= 0.7536 V_{SCE}, can be taken as the exit point; it is a feature of the OsS→SSS2 transient, Fig.1.

Smooth increase of current oscillation amplitudes observed near on the SSS1→OsS transient is shown inFig.2 (a). Linear dependence between the square amplitude of current oscillations (A^2) and increase of the distance of controllable parameter from E_{BIF1} ($|E_{OSC}$-$E_{BIF1}|$) was found, Fig.2 (b). Along with the lack of hysteresis at the SSS1→OsS transient[5] (not shown in abstract),suggests on super-critical Hopf (SUPH) bifurcation[5, 6].

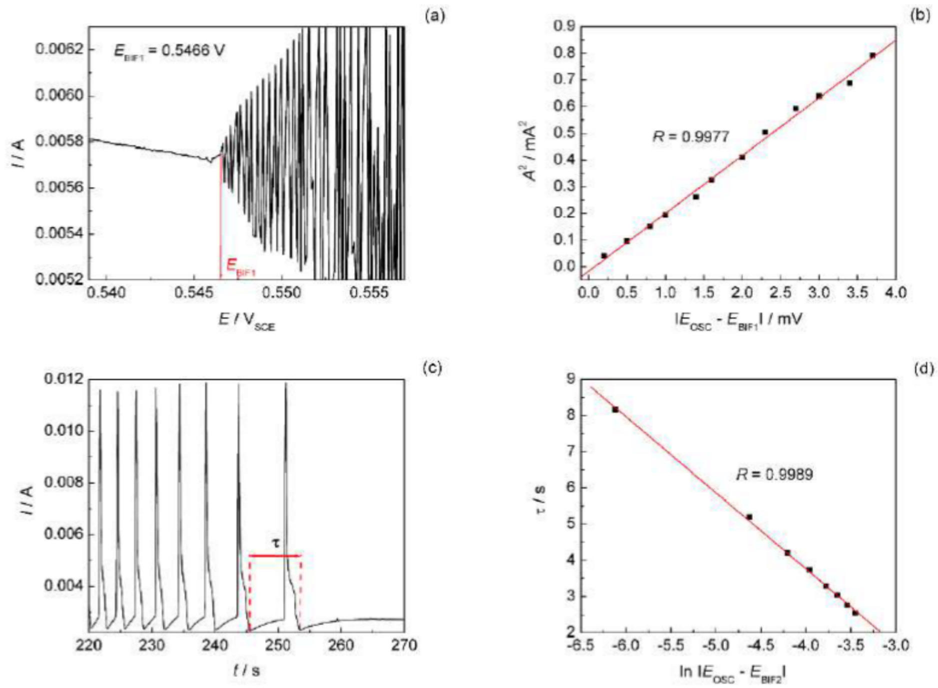

Figure 2. (a) Detail from *I-E* polarization curve, Fig.1, in the vicinity of the SSS1→OsS transient. (b) Dependence of the square amplitude of current oscillations (A^2) vs. distance of controllable parameter from E_{BIF1} ($|E_{OSC}$-$E_{BIF1}|$). (c) Detail from *I-E* polarization curve, Fig.1, in the vicinity of the OsS→SSS2 transient (unites of x-axis are converted from potential to time). (d) Semilogarithmic plot of the period current oscillations (τ) vs. the distance of controllable parameter from E_{BIF2} (ln $|E_{OSC}$-$E_{BIF2}|$).

On the other hand, the period of current oscillations (τ) increases as the system approaches the OsS→SSS2 transient, ending with sudden termination of oscillatory behaviour, Fig.2 (c). Linear dependence between τ and logarithmic value of the distance from E_{BIF2} (ln $|E_{OSC}$-$E_{BIF2}|$) is shown in Fig. 2 (d).Combined with an existence of hysteresis [5] (not shown in abstract), it implies that the OsS→SSS2 transient goes via thesaddle-loop bifurcation[3, 5, 6].Correlation coefficients (*R*),shown in Fig. 2(b) and 2(d),were found to be considerably high. Hence, we can say that the procedure for bifurcation analysis was verified.

CONCLUSION

In this study, a voltammetric data, obtained from qusi-potetiostatic polarization curve of the Cu│1M TFA electrochemical oscillatory system, were used for bifurcation analysis. This was based on the presumption that voltammogram can be considered as a phase space diagram. Results presented have showed that bifurcation scenario can be built from voltammetric data with a high accuracy.

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